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A Journal of Science Communication
VOLUME 4, NO.2, JULY, 2013 & VOLUME 5, NO.1, JANUARY, 2014

Thermochromic Property of Dichromate in Liquid Nitrogen

Dhrubojyoti Chattopadhyay

Abstract

Thermochromism is the reversible colour change of a compound when it is heated or cooled. The thermochromic colour change is distinguished by being quite noticeable, often dramatic and occurring over a small or sharp time interval. It is one of the important phenomena as it has bright future for industrial and practical use. North Bengal Science Centre regularly conducts liquid nitrogen shows for the public to demonstrate the behavior of materials at low temperatures. During the course of such shows it was observed that Ammonium dichromate exhibited thermochromic property at liquid nitrogen temperature possibly because of change in the band gap.

What is Chromism?

Chromophore is a group of atoms within a larger molecule which are principally responsible for the absorption of visible light to give the compound its colour. The colour observed is due to the visible light that is transmitted or reflected by the chromogen. Chromogenic materials change colour in response to electrical, optical (light intensity), thermal changes or with the changes of pH of the solvent. This property of materials is known as Chromism. Accordingly we can categories the chromogenic materials as follows.

Electro-chromic Materials

One of the most useful forms of chromism is electrochromism. This is displayed by the materials which change their colour or opacity with the passage of an electric current or by the presence of a strong electric field. In scientific terms, an electrochromic material is able to reversibly change its colour when it is placed in a different electronic state. So by absorbing an electron (the material concerned is reduced) or by ejecting one (the material is oxidised), it is able to change its colour.

Electrochromism was discovered in 1968 by S. K. Deb and J. A. Chopoorian and has a broad range of commercial applications. Some of those applications are smart windows and mirrors (e.g. darkening a window to control the inlet of sunlight), active optical filters (e.g. sunglasses), displays and computer data storage devices.

Good examples of electrochromic materials are polyanilines which can be formed either by the electrochemical or chemical oxidation of aniline. Depending on the oxidation state, polyaniline can either be pale yellow or dark green/black. Other electrochromic materials that have found technological application include the viologens and polyoxotungstates. Tungsten oxide (WO3), is the main chemical used in the production of electrochromic windows or smart glass.

It is relevant to mention here that there are materials which exhibit a similar phenomenon called electroluminescence. Electroluminescent materials can produce brilliant colors when electrically stimulated. Therefore they are used for decorating buildings and for industrial and public vehicles displays e.g. of safety notices. Examples of electroluminescence are :

- Powdered Zinc Sulfide doped with Copper (producing greenish light) or Silver (producing bright blue light)
- Thin-film Zinc Sulfide doped with Manganese (producing orange-red color)
- Naturally blue diamond, which includes a trace of Boron that acts as a Dopant.
- Semiconductors containing Group III and Group V elements, such as Indium Phosphide (InP), Gallium Arsenide (GaAs), and Gallium Nitride (GaN).
- Certain organic semiconductors, such as $[Ru(bpy)3]2^{+}(PF6)2$, where bpy is 2, 2'-bipyridine

Thermo-chromic Materials

Thermochromism is the change in colour of a material with change in temperature which is reversible in nature. They can be designed to change colour at a particular temperature, which can be varied by doping

the material with other compounds. Thermochromic materials are used to make paints, inks or are mixed to molding or casting materials for different applications.

The most common thermo chromic materials are Liquid Crystals such as Cholesteryl Nonanoate or Cyanobiphenyls. Liquid crystals are used in precision applications, as their responses can be engineered to accurate temperatures, but their color range is limited by their principle of operation. Some liquid crystals are capable of displaying different colors at different temperatures. This change is dependent on selective Bragg diffraction by the crystalline structure of the material, as it changes between the low-temperature crystalline phases, through anisotropic twisted nematic phase, to the high-temperature isotropic liquid phase.

Thermochromic dyes are based on mixtures of leuco dyes with suitable other chemicals, displaying a color change (usually between the colorless leuco form and the colored form) in dependence on temperature. Thermochromic papers are used for thermal printers. Thermochromism can appear in thermoplastics, duroplastics, gels or any kind of coatings. Many inorganic compounds are thermo chromic to some extent. For example, titanium dioxide and zinc oxide are white at room temperature but change to yellow when heated. Similarly normally yellow Indium (III) Oxide darkens to yellow-brown when heated. Lead (II) Oxide exhibits a similar color change on heating. The color change is linked to changes in the electronic properties (energy levels, populations) of these materials. Inorganic compounds that exhibit phase change on heating, exhibits a more dramatic effect. This includes Cuprous mercury iodide (Cu_2HgI_4), Silver Mercury Iodide (Ag_2HgI_4), Bis(diethylammonium) tetrachlorocuprate, etc.

Photo-chromic Materials

The term photochromic is applied to materials whose transmittance to light varies with the intensity of the incident light on it. Photochromic materials reversibly change colour with change in light intensity. Light sensitive sunglasses darken in response to increased intensity of sunlight and so reducing glare e.g. when driving a car or when skiing at high altitude when the snow reflects extra light into your eyes. Light sensitive photochromic materials are used in optical memory devices.

Halo-chromic Materials

Halo-chromic materials change colour according to the pH of the solvent. One possible application is to use paints that can change colour in response to corrosion in the metal underneath them e.g. in the rusting of iron or steel the pH of the water in contact with the metal changes in pH.

Details on thermochromism

Thermochromism was investigated in 1971 at first by two New York inventors, Josh Reynolds and Maris Ambats. In 1975 they bonded liquid crystals with quartz stones and set into rings named "Mood Ring" and claimed that the ring can monitor one's state of mind. The idea that the ring indicates the wearer's mood is based on a claim that body heat fluctuates with the emotional state of the wearer. Human body temperatures are known to vary by small amounts (less than 0.5°C) when the body is fighting an infection or in excitement. But the idea became a flop as the variations in ambient air temperature appear to have a larger effect on the temperature of the ring than changes in the body temperature. However, the invention of the 'Mood Ring' stimulated scientific research. Scientists became interested to know the specific mechanisms of colour change in these materials. Following 4 materials are used in investigating thermochromism.

1. Organic Compounds
2. Inorganic Compounds
3. Polymers
4. Sol-Gels

Thermochromism in Organic Compounds

Advantages of thermochromism for these organic compounds are that their color change takes place sharply and that there are many ways to control temperature easily. It has wide applications for fiber optics, photo storage instruments, optical sensors and so on. The mechanism responsible for thermochromism varies with molecular structure. It may be due to equilibrium between two molecular species, acid-base, keto-enol, lactim-lactam, or between stereoisomers or between crystal structures.

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Thermochromism in Inorganic Compounds

Many metals and inorganic compounds are known to exhibit thermochromic behavior either as solids or in solution. It has been suggested that such thermochromic behavior arises from one of the following mechanisms :

- Phase transition
- Change in ligand geometry
- Equilibrium between different molecular structure
- Change in the number of solvent molecules in the coordination sphere
- Change in the gap between valance band and conduction band

Polymer Thermochromism

Polymer thermochromism arises from polymer planar-non-planar conformation transition. Specially, poly-acetylene is well known as polymer thermochromic material. Generally poly-acetylene can be synthesized in solid state. Color change happens due to transformation of acetylene structure to buta-triene structure.

Sol-gel Thermochromism

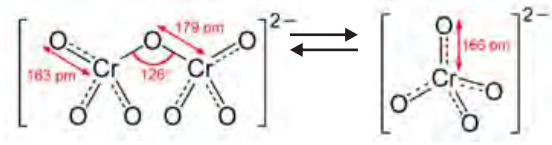
Interactions between macromolecules fall into four categories: ionic, hydrophobic, Van der Waal and hydrogen bonding. Phase transition in polymer gels provides a means of studying these interactions. Many gels will undergo reversible, discontinuous volume changes in response to changes in temperature. This transition results from the competition between repulsive intermolecular forces, usually electrostatic in nature, which act to expand the polymer network, and an attractive force that acts to shrink it.

What exactly happens to Dichromate in liquid Nitrogen ?

Ammonium dichromate is usually orange in colour as its oxidation state is +6. It is observed that if we put a test tube containing aqueous solution of Ammonium dichromate in liquid nitrogen, the color turns to yellow. The yellow state of chromium is +4 i,e, chromate. It is also observed that the reaction is reversible. On withdrawing it from liquid nitrogen the color again turns to orange after sometime.

Initially it was thought that it is a chemical reaction in aqueous solution, as chromate and dichromate anions exist in a chemical equilibrium -

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$



But the question is, according to Le Chatelier's Principle, at low temperature the water will freeze so we should get more dichromate than chromate ion. Ammonium chromate is also a stable compound at room temperature, so the reaction should not be a revisable one. Again we have carried out the same experiment with solid Ammonium dichromate instead of aqueous solution. The same result was obtained. In this case too, solid orange colored materials turn to yellow in low temperature and after some time it again turns in to orange when comes back to normal temperature. Not only that, if we pour liquid nitrogen directly to the solid (which means we carried out the reaction in inert medium, as nitrogen is almost inert in nature) it has shown the same behavior.

Ammonium Dichromate

Ammonium Chromate (?) or Ammonium Dichromate (Courtesy:-Wikipedia)

Therefore, the primary conclusion is that it is not a chemical phenomenon; rather it may be a physical change and the yellow substance, though looks like Ammonium Chromate, is actually Ammonium Dichromate.

To be sure that it is a physical change and not chemical one, we have taken the sample in a test tube and sealed it with grease to make it air tight. Same result was seen in

this case too. Again we have poured liquid nitrogen into the sample and sealed the test tube, so that entire change could take place in an inert atmosphere. Same experiments have been carried out with two different solvents, alcohol and acetone. In all the cases we have observed the same results. Potassium dichromate also shows a similar result. So it is confirmed that dichromate shows thermochromism at low temperature as a result of physical change.

Conclusion

It has been found by scientists that a mixture of Chromium (III) oxide and Aluminium (III) oxide in 1:9 ratio is red at room temperature and grey at 400 °C, due to changes in its crystal field. In our experiment, the dichromate compounds showed distinct colour changes when cooled. In most of the cases thermochromic behavior is shown due to phase transition or changes in ligand geometry, but here the most possible cause is due to change in energy gap between valance band and transition band or due to inner orbital electron rearrangement. However, a detailed analysis is required to confirm the hypothesis.

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Dhrubojyoti Chattopadhyay, Education Officer
North Bengal Science Centre, Siliguri
Post Matigara, Siliguri - 734010, Dist. Darjeeling
Email : nbscsiliguri@bsnl.in